⑫ EUROPEAN PATENT APPLICATION

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�54 **A coil coating paint composition.**

㊗ A coil coating composition consisting essentially of (A) a binder component comprising a mixture of a linear polyester resin and a branched polyester resin, having a hydroxyl value of 40 to 90, and (B) a crosslinking component selected from melamine resin, at least part of which is methyl methylolated melamine, or isocyanate compound. Said polyester resins are herein defined.

The coating composition is useful in a coil coating and results a coating with excellent properties in respect of hardness, bending processability, fastness to boiling water, weather resistance, chemical resistance, marker stain resistance and the like.

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A coil coating paint composition

The present invention relates to a coil coating paint composition. More specifically, the invention concerns a high solids coating composition for coil coating use, capable of forming a coating with excellent properties in respect of hardness, bending processability, fastness to boiling water, weather resistance, chemical resistance, marker stain resistance and the like.

5   As a coating composition to be used in a coil coating of steel plate and the like, various properties including excellent weather resistance, chemical resistance, water resistance, coin scratch resistance, gloss, hardness, and bending properties of the coating, as well as the capability of formulating a high solids paint.

In such application, a polyester resin is a promising material because of resulting a coating with excellent weather resistance, chemical resistance, hardness and the like. However, this material has a
10   serious drawback of lacking in structural flexibility. As an attempt for giving strechability and flexibility to a polyester resin, has been proposed a technique wherein a comparatively long methylene chain is included in either of dicarboxylic acio or diol component or in lactone to be reacted with polyester resin, thereby introducing the same into the polyester's molecular structure. However, haroness and bending properties are, in principle, contrary to each other, and an improvement in flexibility is always linked with the decrease
15   in hardness. Thus, it is quite difficult to attain the well balanced flexibility and hardness in a single polyester resin.

It has also been proposed to use a mixture of soft polyester and hard polyester as a binder resin (Japanese Patent Application Kokai No. 111864/83, ibid 111865/83). In these attemps, while maintaining hardness, water resistance and chemical resistance each in an appropriate level, it was indeed succeeded
20   in having an improved flexibility, rubber-like elasticity and the like by the control of methylene chain content of the resinous composition, but it was only settled to the mere satisfaction of the desired properties of the coating on soft materials as fender, bumper and the like. The proposed coating compositions were of quite dissatisfaction when used as a coil coating of steel plate especially with respect to hardness, bending properties and the like.

25   Recently, a very attractive lacquer type coil coating paint composition has been proposed in Japanese Patent Application Kokai No. 210975/84, in which a linear polyester resin having a number average molecular weight of 15,000 to 50,000 and a linear or branched polyester resin having a number average molecular weight of 2,000 to 10,000 are mixed in a weight ratio of 80:20 to 20:80 and used as a resinous binder. The said composition is said to give a coating with well balanced hardness and bending
30   processability.

However, since the coating composition does not include any crosslinking agents, the thus formeo coating is insufficient in weather resistance, fastness to boiling water, chemical resistance and the like. Even if a crosslinking agent is tried to be blendeo with said coating composition, an aoditional problem of poor compatibility woulo be inevitably arisen from the high molecular weight of the polyester resin used.

35   Therefore, the application of said lacker type paint composition is in fact confined in limited areas.

An object of the present invention is therefore to provide a polyester binder which is compatible with a crosslinking agent. An additional object of the invention is to provide a coating composition for coil coating use, which will give the coating with well balanced hardness and bending processabilities, as well as the characteristic properties possessed by polyester resin, and capable of being formulated as a high solids
40   paint.

The inventors, as the results of extensive studies, have found that if a melamine resin at least part of which is methyl methylolated melamine (e.g. methylol melamine methyl ether alone or a mixture of methylol melamine methyl ether and methylol melamine butyl ether) or an isocyanate compound is selected as a crosslinking agent and a combination of low molecular weight (up to number average molecular weight
45   5000) linear polyester and a branched polyester is used as binder resins, a compatible blend can be formulated and a high solids coating composition capable of resulting a coating with well balanced hardness and bending processability can be obtained. On the basis of these findings, the present invention has been made.

Thus, according to the invention, is provided a coating composition for coil coating use consisting
50   essentially of

(a) a binder component comprising a mixture of a linear polyester resin and a branched polyester resin, having a hydroxyl value of 40 to 90, said linear polyester resin being composed of polybasic acid component and polyhydric alcohol component consisting of trihydric and/or polyhydric alcohol (0 to 10wt% of the solid matter) and dihydric alcohol and having 1.8 to 2.2 hydroxyl groups per molecule and a number

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average molecular weight of 1000 to 5000, and said branched polyester resin being composed of polybasic acid component and polyhydric alcohol component consisting of trihydric and/or tetrahydric alcohol (3 to 40 weight% of the solid matter) and dihydric alcohol, and having 2.3 to 4.5 hydroxyl groups per molecule, and

(B) a crosslinking component consisting of melamine resin, at least part of which is a methyl methylolated melamine, or isocyanate compound.

The first polyester resin used in the present invention is an oil-free linear polyester resin composed of polybasic acid component and polyhydric alcohol component, the polyhydric alcohol component consisting of substantial amount of dihydric alcohol and a small amount (0 to 10 weight % of the solid matter) of trihydric and/or tetrahydric alcohol, having 1.8 to 2.2 hydroxyl groups per molecule and a number average molecular weight 1000 to 5000. By the employment of this type of polyester resin, entanglement of resinous molecules and physical crosslinking are of use in giving improved hardness, weather resistance and fastness to boiling water of the coating, and easy unraveling properties of the entangled molecules, sliding properties and stress relaxation are believed to be of use in giving improved bending properties and low temperature impact strength. When the hydroxyl groups are less than 1.8 per molecule, there remains a considerable number of unreacted chains, which will cause the decrease in weather resistance of the coating, whereas if the hydroxyl groups exceed over 2.2 per molecule, there will cause the decrease in sliding properties and hence the desired bending properties.

The number average molecular weight of said linear polyester resin should be in a range of 1000 to 5000, and preferably 2000 to 4000. This is because, in the combination of said resin with the specified crosslinking agent and branched polyester resin, if the number average molecular weight of said linear polyester is less than 1000, it is unable to expect the desired bending processability, and if it exceeds over 5000, it is unable to have a high solids coating composition and the desired compatibility with the selected crosslinking agent.

The second polyester resin used in the present invention is a branched, oil-free polyester resin composed of polybasic acid component and polyhydric alcohol component consisting of trihydric and/or tetrahydric alcohol, the hydroxyl groups number per molecule being 2.3 to 4.5. By the selective use of this type of branched polyester resin, hardness, weather resistance and fastness to boiling water of the coating are greatly improved because of the increase in chemical crosslinking between the functional groups contained therein.
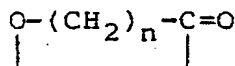
If the hydroxyl group number is less than 2.3, it is unable to obtain the desired hardness and weather resistance of the coating, whereas the preparation of branched polyester resin having more than 4.5 hydroxyl groups per molecule is very difficult to do.

In the present invention, the abovementioned linear polyester resin and branched polyester resin are mixed together so as to give a hydroxyl value of 40 to 90. This is because, if the hydroxyl value of the mixed resin is less than 40, the formed coating is too soft to the objects of the invention, and if it exceeds over 90, the coating is too hard.

As to the number average molecular weight of said branched polyester resin, it is not so critical to the objects of the invention and is approriately selected in a common range of about 800 to 4000.

The present branched polyester resin may be modified with a lactone of the formula:

$$O-(CH_2)_n-C=O$$

wherein n is an integer of 4 to 10, thereby giving softness to the branched polyester resin and increasing crosslinking density of the cured coating, if desired. Said lactone may be used in an amount of 0 to 40 weight% of the resin solid. Further more, in the present invention, either or both of the abovementioned linear and branched polyester resins may be modified with an alkyleneimine as, for example, N-(2-hydroxy ethyl) ethyleneimine (HEEI) to improve pigment dispersion properties of the resin composition.

As already stated, the most characteristic feature of the invention resides in the point that the abovementioned resin composition is used as a binder component together with a crosslinking agent selected from the group consisting of a melamine resin at least part of which is methyl methylolated melamine, and an isocyanate compound.

Contrary to our expectations, number average molecular weight of the linear polyester resin to be blended with a branched polyester resin could be markedly lowered when the abovesaid particular compound was selectively used as a crosslinking agent.

At present, the exact reasons have not been fully understood, but the following are presumed to be one of the grounds thereof.

That is, when said crosslinking agent is selected, differing from the case with butylated melamine, the self condensation of the crosslinking agent is prevented and the resin and the crosslinking agent are reacted with each other in alternative order to give a soft, cured coating.

Lowering of the molecular weight of the polyester resin contributes to the improvement in the compatibility of said resin with a crosslinking agent and to the formation of a high solids coating composition. Employment of said polymer blend can result well balanced properties of hardness and bending processability, and employment of said crosslinking agent far improvements in weather resistance, fastness to boiling water, chemical resistance and marker stain resistance of the coating. Thus, the present composition is very useful as a resinous vehicle of a coil coating paint composition.

As to the blending ratio of the abovementioned polyester resins, it is selected in a wider range depending on the application desirec. The polyester blend is preferably compounded with the abovementioned crosslinking agent in a weight ratio (as solid) of 5/95 to 50/50, most preferably 20/80 to 35/65.

The present coating composition is usually applied on a steel plate or the like by coil coating means and baked, in most cases, at 180 to 250°C for 30 seconds to 2 minutes to give a coating with excellent properties with respect to hardness, bending properties, weather resistance, gloss, coin scratch resistance, fastness to boiling water, chemical resistance and marker stain resistance.

The invention shall be now more fully explained in the following Examples. Unless otherwise being stated, all parts and % are by weight.

Synthetic Example 1

Preparation of linear polyester resin (A)

Into a 2 liters reaction vessel fitted with a stirrer, a fractionating column, a nitrogen gas inlet tube and a thermometer, were placed 140.9 parts of terephthalic acid, 495.5 parts of adipic acid, 135.9 parts of ethyleneglycol, 227.8 parts of neopentylglycol and 2 parts of dibutyl tin oxide and the mixture was heated. At the stage when it was reached to a stirrable condition, stirring was commenced to start and the temperature was raised to 240°C. At that time, from 160°C to 240°C, the temperature was raised at a constant speed in 3 hours. The raction water formed was continuously distilled off through the fractionating column out of the system. When the temperature was reached to 240°C, the mixture was maintained at said temperature and stirred for 1 hour. Thereafter, the fractionating column was stopped from working, xylene was added and the mixture was further reacted under refluxing conditions. When the acid value of the reaction product was reached to about 2.0, the reaction was overed and the mixture was allowed to cool. After cooling, 214 parts of xylene and 214 parts of Cellosolve acetate were added to obtain an oil-free polyester resin solution A-①. Analysis showed that it had a solid content of 70.4%, a viscosity (Gardner bubble viscometer, 25°C) of Y and contained polyester resin having a number average molecular weight of 5,000, a hydroxyl value of 21, an average number of hydroxyl groups per molecule of 1.8 and an acid value of 2.1.

Synthetic Examples 2 to 5

Following the procedures of Synthetic Example 1 but using the materials shown in Table 1, various linear polyester resins were prepared. However, in these Examples, a light modification was made as follows. That is, in the cases of the resins A-④ and A-⑤, the condensation reactions were stopped at the stage when the acid value (AV/NV) was reached to 7.0 and 5.0, respectively, and the reaction mixture was allowed to cool to 90°C. While keeping the temperature at 90°C, 7.0 parts (in the case of A-④) and 4.3 parts (in the case of A-⑤) of N-(2-hydroxyethyl)ethyleneimine (HEEI) were added and the mixtures were reacted for 1 hour and then diluted with a mixture of 269 parts of xylene and 269 parts of Cellosolve acetate, respectively. The characteristics of these resin varnishes are shown in Table 1.

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Synthetic Example 6

Preparation of branched polyester resin (B)

5   Into a similar reaction vessel as used in Synthetic Example 1, were placed 373.9 parts of isophthalic acid, 85.6 parts of hexahydrophthalic anhydride, 94.6 parts of 1,6-hexanediol, 81.1 parts of neopentylglycol, 103.6 parts of trimethylol propane, 229.7 parts of Cardula E-10, and 2 parts of dibutyl tin oxide and the mixture was heated. At the stage when it was reached to a stirrable condition, stirring was commenced to start and temperature was raised to 230°C. At that time, from 195°C to 230°C, temperature was raised at a
10   constant speed in 2 hours. Thereafter, the reaction was continued as in Synthetic Example 1 until the acid value of the reaction product was reached to about 3.0. After cooling to 150°C, the mixture was added with 31.5 parts of phthalic anhydride and reacted to obtain an oil-free polyester resin solution. The characteristics of thus obtained varnish are shown in Table 1.

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Synthetic Example 7

     Into a similar reaction vessel as used in Synthetic Example 1, were placed 274.0 parts of isophthalic acid, 255 parts of hexahydrophthalic anhydride, 178.3 parts of 1,6-hexanediol, 157.1 parts of neopentyl-
20   glycol, 61.5 parts of trimethylol propane, 73.8 parts of caprolactam and 2.0 parts of dibutyl tin oxide and the mixture was reacted as in Synthetic Example 1 until the resinous acid value was reached to about 15. After cooling, the mixture was added with 269 parts of xylene and 269 parts of Cellosolve acetate to obtain a resin varnish. The characteristics of thus obtained varnish are shown in Table 1.

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Synthetic Example 8

     Repeating the same procedures as stated in Synthetic Example 7 but using the materials shown in Table 1, an oil-free polyester resin varnish was prepared, whose characteristics were also shown in Table 1.
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Synthetic Example 9

     Into a similar reaction vessel as used in Synthetic Example 1, were placed 288.1 parts of isophthalic
35   acid, 67.1 parts of hexahydro phthalic anhydride, 94.6 parts of neopentylglycol, 124.9 parts of trimethylol-propane, 182.9 parts of Cardula E-10 and 207.2 parts of ε -caprolactam and the mixture was reacted as in Synthetic Example 1. As soon as the resinous acid value was reached to about 7.0, the reaction was stopped and the reaction mixture was allowed to cool to 140°C. 35.3 parts of phthalic anhydride were added and the mixture was further reacted to obtain an oil-free polyester resin varnish. The characteristics
40   of thus obtained varnish are shown in Table 1.

Synthetic Examples 10 to 12

45   Repeating the same procedures as stated in Synthetic Example 1 but using the materials shown in Table 1, branched polyester resin varnishes were prepared. The characteristics of thus obtained varnishes are shown in Table 1.

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Synthetic Example 13

Preparation of Comparative resin varnish C- (13)

5   Into 2 liters reaction vessel which was similar to that of Synthetic Example 1 and was connected to a
vacuum pump, were placed 244.9 parts of terephthalic acid, 244.9 parts of isophthalic acid, 298.3 parts of
sebacic acid, 138.4 parts of ethyleneglycol, 232.4 parts of neopentylglycol , 2 parts of bibutyl tin oxide and
2 parts of antimony trioxide and the mixture was reacted at 170 to 250°C. After completion of the
esterification reaction, polycondensation reaction was carried out under reduced pressure of 0.5 to 1.0
10   mmHg to obtain a high molecular weight linear polyester resin. The characteristics of thus obtained resin
varnish are shown in Table 1.

Synthetic Example 14

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Preparation of Comparative resin varnish C- (14)

Repeating the same procedures as stated in Synthetic Example 1 but using the materials shown in
Table 1, a low molecular weight linear polyester resin varnish was prepared. The characteristics of said
20   resin varnish are shown in Table 1.

Synthetic Example 15

25   Preparation of Comparative resin varnish C- (15)

Repeating the same procedures as stated in Synthetic Example 1 but using the materials shown in
Table 1, a linear polyester resin varnish was prepared. The characteristics of thus obtained varnish are
shown in Table 1.

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Synthetic Examples 16 and 17

Preparation of Comparative resin varnishes C-(16) and C-(17)
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Repeating the same procedures as stated in Synthetic Example 1 but using the materials shown in
Table 1, branched polyester reisn varnishes were prepared. The characteristics of these varnished are
shown in Table 1.
In the following Example, a number average molecular weight of a polyester resin is calculated by the
40   equation: (as prescribed in "A guide to synthetic resins for coating use" written by Kyozo Kitaoka, published
by High Molecular Publishing Associate, page 101)

$$M_n = \frac{W}{(ma + mb) - (1 - \frac{\alpha}{100}) \, ea_2 - ea_1 + \frac{W - AV}{56100}}$$

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wherein
α : intramolecular reaction rate % (in case of phthalic anhydride ... 4.0)
W : weight of final resin
50
ma : number of moles of acid in the final resin
mb : number of moles of alcohol charged
ea_2 : equivalent of acid charged
ea_1 : equivalent of monobaric acid charged
AV : acid value of final resin
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Example 1

A coil coating composition was prepared by kneading the following mixture in a ball mill for 24 hours. The oil-free polyester resins A- ① and B- ⑥ used are shown in Synthetic Examples 1 and 6 respectively.

Formulation:

70.4% linear polyester resin A-①	71.4 parts
65.0% branched polyester resin B-⑥	76.9
80% methyl methylolated melamine [1]	37.5
titanium oxide [2]	100.0
p-toluene sulfonic acid solution [3]	6.5
Modaflow [4]	0.3
n-butanol	15.0
	Total 307.6

1) Sumimal M-40S, non-volatile content 80%, trade mark, Sumitomo Chem. Co.
2) Titanium CR-91, trade mark, Ishihara Sangyo
3) 20 wt% benzylalcohol solution>
4) trade mark, Monsanto Cem. Co.

Thus obtained composition was added with a dilution thinner: 1:1 (by weight) = Solvesso 150 : Isophorone
to give a diluted composition having a viscosity of 120 seconds (Ford Cup #4, at 20°C).

The diluted coating composition was then applied on a galvanized steel having a thickness of 0.3mm (JIS-G3302) previously treated with a zinc phosphate solution, to give a wet film thickness of 10 to 15μ and the coated steel plate was baked at 230°C for 40 seconds.

The following tests were carried out with the coating composition and with the coated plate.

1) non-volatile content (%) of the coating composition

A coating composition was diluted with a mixed dilution thinner (isophorone/Solvesso #150 = 1/1 wt/wt) to a viscosity (#4 Ford cup, at 25°C) of 120 seconds. An amount of said composition was taken and weighed, and after being subjected to a drying at 105°C for 3 hours, the residual amount was again weighed and non-volatile content of said composition was calculated therefrom.

2) gloss

60° reflextion factor was ditermined by using Murakami type GM-3H glossmeter.

3) Pencil hardness

Pencil hardness was determined by using a high quality pencil prescribed by JIS-S-6006 and following a standardized method of JIS-K-5400

4) bending properties

A coated steel was folced at 180° and cracking behavior at the bended portion was observed.
2T, for example, stands for no cracking when two coated plates having the same thickness are bended
together.

5) fastness to boiling water

A coated plate was dipped in a boiling water for 8 hours, and the coating was then observed.
O... good ×... no good (generation of blister)

6) chemical resistance

0.5cc of 10% aq. H_2SO_4 solution was dropped on a coated surface and the plate was maintained at
20°C and under 75% relative humidity (RH) condition for 24 hours. Thereafter, the coating was washed with
water and chemical resistance of the coating was determined.
O... good ×... no good

7) marker stain resistance

A red colored oil ink was applied on the coating (in 0.5x2cm area) and after leaving it at 20°C for 24
hours, the inked area was scrubbed with a gauze impregnated with methanol and observed the degree of
stain
O... good ×... no good

8) weather resistance

Gloss retention (%) was measured after 2000 hours' irradiation in Sunshine weather-O-meter.
The test results are shown in Table 2.

Example 2 and 3

Using the linear polyester resins A-② and A-③ and the branched polyester resins B-⑦ and B-⑧,
the same procedures as stated in Example 1 were repeated to obtain coating compositions. The respective
coating composition was diluted, applied on the similar galvanized steel, baked and tested as in Example 1.
The test results are shown in Table 2.

Example 4

A coil coating composition was prepared by using the oil-free polyester resin A-④ and B-⑨ obtained
in Synthetic Examples 4 and 9, and following the dispersion formulation (1) and solution formulation (2)
hereinunder stated.

Dispersion formulation (1)

        65.2% linear polyester resin A-④   46.2 parts

        titanium oxide   100.0

        n-butanol   15.0

                                      Total 161.2

Solution formulation (2)

      Dispersion paste

      (of dispersion formulation (1))   161.2 parts

      65.0% branched polyester resin B-⑨   108

      80% methyl methylolated melamine   37.5

      p-toluene sulfonic acid solution   6.5

      Modaflow   0.3

                                      Total 273.0

Thus obtained coating composition was diluted, applied on a galvanized steel previously treated with a zinc phosphate solution and baked as in Example 1.
    The same tests as stated in Example 1 were carried out and the test results were shown in Table 2.

Examples 5 and 6

    Using the oil-free polyester resins A- ④ and B-⑩ obtained in Synthetic Examples 4 and 10 in Example 5, and the oil-free polyester resins A- ⑤ and B-⑧ obtained in Synthetic Examples 5 and 8 in Example 6, the same procedures as stated in Example 4 were repeated to obtain coating compositions. They were diluted, applied on galvanized steel plates previously treated with a zinc phosphate solution, baked and tested as in Example 1. The test results are shown in Table 2.

Examples 7 and 8

    Using the oil-free polyester resins A- ② and B- ⑪ obtained in Synthetic Examples 2 and 11 in Example 7 and the oil-free polyester resins A-③ and B-⑫ obtained in Synthetic Examples 3 and 12 in Example 8, together with an amount of methyl methylolated melamine shown in Table 2, the same procedures as stated in Example 1 were repeated to obtain coating compositions. They were diluted, applied on galvanized steel plates previously treated with a zinc phosphate solution, baked and tested as in Example 1. The test results are shown in Table 2.

Example 9

A coil coating composition was prepared by using the oil-free polyester resins A- ① and B-⑥ obtained in Synthetic Examples 1 and 6 and Following the prescription metnioned below:

70.4% linear polyester resin A-①	85.2 parts
65.0% branched polyester resin B-⑥	61.5
80% methyl methylolated melamine	26.3
60% butyl methylolated melamine [1]	15
titanium oxide	100
p-toluene suflonic acid soltion	3.0
Modaflow	0.3
n-butanol	15.0
Total	306.3

[1] ... Super Beckamine J-820-60, trade mark, Dainippon Ink Chem. Ind. Ltd., non-volatile content 60%

Thus obtained coating composition was diluted, applied on a galvanized steel plate previously treated with a zinc phosphate solution, baked and tested as in Example 1. The test results are shown in Table 2.

Example 10

Using the oil-free polyester resins A- ② and B- ⑦ obtained in Synthetic Examples 2 and 7 and the melamine resins shown in Example 9, the same procedures as stated in Example 9 were repeated to obtain a coating composition. The composition was diluted, applied on a galvanizeo steel plate previously treated with a zinc phosphate solution, baked and tested as in Example 1.
The test results are shown in Table 2.

Example 11

A coil coating composition was prepared by using the oil-free polyester resins A-②and B- ⑪obtained in Synthetic Examples 2 and 11 and following the prescriptions shown below.

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        Dispersion formulation (1)

            70.2% linear polyester resin A-②    42.7 parts

            titanium oxide                       100.0
                                                 _____

                                          Total  142.7

    Solution formulation (2)

        Dispersion paste
        (of disperion formulation (1))           142.7 parts

        70.2% linear polyester resin A-②         71.2

        65.2% branched polyester resin B-⑪       30.7

        Sumidule N-75 1)                         16.0

        dibutyl tin dilaurate                    0.02

        Modaflow                                 0.5
                                                 _____

                                          Total  261.1
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1)... 75% aliphatic polyisocyanate in 1:1 Cellosolve

acetate/xylene, trade mark, Sumitomo Bayer Urethane K.K.

Thus obtained coating composition was diluted, applied on a galvanized steel plate previously treated with a zinc phosphate solution, baked and tested as in Example 1. The test results are shown in Table 2.

Comparative Examples 1 to 9

Comparative coating compositions 1 to 9 were prepared by using the same procedures as stated in Example 1 and the materials shown in Table 2. They were diluted, applied on a galvanized steel plate previously treated with a zinc phosphate solution, baked and tested as in Example 1. The test results are also shown in Table 2.

Table 1 (continued)

linear type polyester resin

Synthetic Example	1	2	3	4	5
oil-free polyester resin	A-①	A-②	A-③	A-④	A-⑤
Composition and characteristics					
resin specifications					
a. number average molecular weight	5,000	3,000	2,500	2,000	1,200
b. OH value	21	35	45	62	94
c. average OH number per molecule	1.8	1.9	2.0	2.2	2.0
d. trivalent/tetravalent alcohol (wt%)	0	0	0.4	7.8	4.3
e. ε-caprolactone (wt%)	—	—	—	—	—
characteristics of resin					
A. non-volatile content (%)	70.4	70.2	69.8	65.2	65.0
B. viscosity (25°C Gardner)	Y	Z_1	Y	XY	T
C. acid value (AV/NV)	2.1 / 2.0	2.0 / 2.0	2.0 / 2.0	2.1 / 2.0	2.2 / 2.2

Table 1 (continued)

branched type polyester resin

Synthetic Example	6	7	8	9	10
oil-free polyester resin	B-⑥	B-⑦	B-⑧	B-⑨	B-⑩
Composition and characteristics					
resin raw materials					
1. terephthalic acid					
2. isophthalic acid	373.9	274.0	455.5	288.1	205.7
3. phthalic anhydride					
4. adipic acid					120.6
5. azelaic acid					
6. sebacic acid					
7. hexahydro phthalic anhydride	85.6	255.2		67.1	
8. ethyleneglycol					
9. 1,4-butanediol					
10. 1,6-hexanediol	94.6	178.3	119.9		
11. neopentyl glycol	81.1	157.1	160.0	94.6	156.6
12. trimethylol propane	103.6	61.5	52.1	124.9	116.8
13. pentaerythritol					
14. Cardura E-10	229.7			182.9	
15. ε-caprolactone(n=5)		73.8	212.5	207.2	400.0
16. phthalic anhydride (for later charge)	31.5			35.3	
17. 2-hydroxyethyl ethyleneimine (HEEI)					

Table 1 (continued)

branched type polyester resin

Synthetic Example	6	7	8	9	10
oil-free polyester resin	B-⑥	B-⑦	B-⑧	B-⑨	B-⑩
Composition and characteristics					
resin specifications					
a. number average molecular weight	1,800	2,200	3,000	1,900	2,000
b. OH value	91	64	55	93	98
c. average OH number per molecule	3.0	2.5	2.9	3.2	3.5
d. trivalent/tetravalent alcohol (wt%)	10.4	6.2	5.2	12.5	11.7
e. ε-caprolactone (wt%)	0	7.4	21.2	20.7	40.0
characteristics of resin					
A. non-volatile content (%)	65.1	64.8	65.2	65.0	65.1
B. viscosity (25°C Gardner)	Y<Z	$Z_1 < Z_2$	W-X	Y	XY
C. acid value (AV/NV)	15.0	15.1	7.3	20.2	10.0

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Table 1 (continued)

branched type polyester resin

Synthetic Example	11	12
oil-free polyester resin	B-⑪	B-⑫
Composition and characteristics		
resin raw materials		
1. terephthalic acid		
2. isophthalic acid	303.9	365.6
3. phthalic anhydride		
4. adipic acid	178.2	214.4
5. azelaic acid		
6. sebacic acid		
7. hexahydro phthalic anhydride		
8. ethyleneglycol		
9. 1,4-butanediol		
10. 1,6-hexanediol	62.8	207.3
11. neopentyl glycol	55.4	182.8
12. trimethylol propane	399.7	30.0
13. pentaerythritol		
14. Cardura E-10		
15. ε-caprolactone(n=5)		
16. phthalic anhydride (for later charge)		
17. 2-hydroxyethyl ethyleneimine (HEEI)		

Table 1 (continued)

branched type polyester resin

Synthetic Example	11	12
oil-free polyester resin	B-⑪	B-⑫
Composition and characteristics		
resin specifications		
a. number average molecular weight	800	4,000
b. OH value	315	32
c. average OH number per molecule	4.5	2.3
d. trivalent/tetravalent alcohol (wt%)	39.9	3.0
e. ε-caprolactone (wt%)	0	0
characteristics of resin		
A. non-volatile content (%)	65.2	65.1
B. viscosity (25°C Gardner)	UV	Z_1
C. acid value (AV/NV)	10.0	10.0

Table 1 (continued)

comparative resin

Synthetic Example	13	14	15	16	17
oil-free polyester resin	C-⑬	C-⑭	C-⑮	C-⑯	C-⑰
Composition and characteristics					
resin raw materials					
1. terephthalic acid	244.9				
2. isophthalic acid	244.9	317.0	284.6	166.5	247.6
3. phthalic anhydride			104.9		147.2
4. adipic acid		278.9	250.4	97.6	145.2
5. azelaic acid					
6. sebacic acid	298.3				
7. hexahydro phthalic anhydride					
8. ethyleneglycol	138.4	150.8	134.3		
9. 1,4-butanediol					
10. 1,6-hexanediol					
11. neopentyl glycol	232.4	253.4	225.8	114.7	100.2
12. trimethylol propane				118.6	113.7
13. pentaerythritol					246.1
14. Cardura E-10					
15. ε-caprolactone(n=5)				502.7	
16. phthalic anhydride (for later charge)					
17. 2-hydroxyethyl ethyleneimine (HEEI)					

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Table 1 (continued)

comparative resin

Synthetic Example oil-free polyester resin	13	14	15	16	17
Composition and characteristics resin	C-⑬	C-⑭	C-⑮	C-⑯	C-⑰
resin specifications					
a. number average molecular weight	20,000	800	3,000	2,000	1,800
b. OH value	6.0	138	28	98	155
c. average OH number per molecule	2.0	2.0	1.5	3.5	5.0
d. trivalent/tetravalent alcohol (wt%)	0	0	0	11.9	24.6
e. ε-caprolactone (wt%)	—	—	—	50.3	—
characteristics of resin					
A. non-volatile content (%)	40.2	70.2	70.1	65.1	65.4
B. viscosity (25°C Gardner)	—	XY	Y-Z	X	Z_6<
C. acid value (AV/NV)	2.0	2.0	2.0	10.0	10.0

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Table 2

Example	1	2	3	4	5	6
resin formula						
linear type polyester resin	A-①	A-②	A-③	A-④	A-④	A-⑤
solid	50	50	30	30	30	50
branched type polyester resin	B-⑥	B-⑦	B-⑧	B-⑨	B-⑩	B-⑧
solid	50	50	70	70	70	50
OH value of blend	56	50	52	65	87	74
methylolated melamine resin (solid)	30	30	30	30	30	30
butylated melamine (solid)						
MeMF/BuMF (solid)						
isocyanate (Sumidul N-75)						
Test results						
non-volatile content(%) of coating composition	70.8	70.5	70.5	70.6	70.1	70.6
gloss	91.2	89.5	92.0	90.1	88.9	90.1
pencil hardness	2H	2H	2H	2H~3H	3H	2H
bending properties	2T	2T~3T	3T	3T	3T	3T
fastness to boiling water	○	○	○	○	○	○
chemical resistance	○	○	○	○	○	○
marker stain resistance	○	○	○	○	○	○
weather resistance	82	85	80	82	79	80

Table 2 (continued)

Example	7	8	9	10	11
resin formula					
linear type polyester					
resin	A-②	A-③	A-①	A-②	A-②
solid	90	80	60	40	80
branched type polyester					
resin	B-⑪	B-⑫	B-⑥	B-⑦	B-⑪
solid	10	20	40	60	20
OH value of blend	63	42	49	52	89
methylolated melamine					
resin (solid)	15	35	21	15	
butylated melamine (solid)			9	15	
MeMF/BuMF (solid)			70/30	50/50	
isocyanate (Sumidul N-75)					16.7
Test results					
non-volatile content(%)					
of coating composition	70.2	71.2	70.1	70.2	71.3
gloss	90.2	90.5	88.6	88.3	90.2
pencil hardness	2H	3H	2H	2H	2H
bending properties	1T~2T	3T	2T	3T	2T
fastness to boiling water	○	○	○	○	○
chemical resistance	○	○	○	○	○
marker stain resistance	○	○	○	○	○
weather resistance	80	82	80	81	85

(handwritten annotation: zeigt, daß Vernetzer relativ eq. ist)

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Table 2 (continued)

Comp.Example	1	2	3	4	5
resin formula					
linear type polyester					
resin	C-⑬	C-⑭	C-⑮	A-①	A-④
solid	40	40	20	80	20
branched type polyester					
resin	B-⑨	B-⑧	B-⑧	B-⑥	B-⑩
solid	60	60	80	20	80
OH value of blend	58	88	50	35	113
methylolated melamine					
resin (solid)	30	30	30	30	30
butylated melamine (solid)					
MeMF/BuMF (solid)					
isocyanate (Sumidul N-75)					
Test results					
non-volatile content(%)					
of coating composition	55.7	70.3	70.1	70.3	70.3
gloss	63.2	88.4	89.2	88.3	85.3
pencil hardness	B	2H	2H	2H	2H
bending properties	1T	6T	3T	2T	6T~7T
fastness to boiling water	×	×	×	×	○
chemical resistance	×	○	×	×	○
marker stain resistance	×	○	×	×	○
weather resistance	62	50	42	43	69

Table 2 (continued)

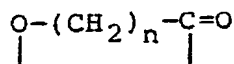| Comp. Example	6	7	8	9
resin formula				
linear type polyester resin	A-④	A-③		A-④
solid	40	100		80
branched type polyester resin	C-⑯		B-⑦	C-⑰
solid	60		100	20
OH value of blend	84	45	64	81
methylolated melamine resin (solid)	30	30	30	30
butylated melamine (solid)				
MeMF/BuMF (solid)				
isocyanate (Sumidul N-75)				
Test results				
non-volatile content(%) of coating composition	70.6	70.5	70.3	65.3
gloss	87.2	80.2	88.1	*
pencil hardness	HB	2B	3H	2H
bending properties	2T	1T	10T<	3T
fastness to boiling water	○	×	○	×
chemical resistance	○	×	○	×
marker stain resistance	○	×	○	×
weather resistance	78	45	79	62

*....loss in gloss

Claims

1. A coating composition for coil coating use consisting essentially of

(A) a binder component comprising a mixture of a linear polyester resin and a branched polyester resin, having a hydroxyl value of 40 to 90, said linear polyester resin being composed of polybasic acid component and polyhydric alcohol component consisting of trihydric and/or tetrahydric alcohol (0 to 10 wt% of the solid matter) and dihydric alcohol, and having 1.8 to 2.2 hydroxyl groups per molecule and a number average molecular weight of 1000 to 5000, and said branched polyester resin being composed of polybasic acid component and polyhydric alcohol component consisting of trihydric and/or tetrahydric alcohol (3 to 40 wt% of the solid matter) and dihydric alcohol, and having 2.3 to 4.5 hydroxyl groups per molecule, and

(B) a crosslinking component consisting of melamine resin, at least part of which is a methyl methylolated melamine, or isocyanate compound.

2. A composition according to claim 1 wherein the branched polyester resin is modified with a lactone of the formula:

$$O-(CH_2)_n-C=O$$

wherein n is an integer of 4 to 10.

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X	US-A-3 345 429 (WESTINGHOUSE ELECTRIC CORP.) * Claims 4-6 *	1	H 01 B 3/30
A	CHEMICAL ABSTRACTS, vol. 94, 1981, page 90, abstract no. 210367s, Columbus, Ohio, US; F.T. NOUWENS: "High solids industrial coatings", & CONGR. FATIPEC 1980, 15th(2), II-270-II-280 * Abstract *	1,2	
A	CHEMICAL ABSTRACTS, vol. 83, no. 4, 28th July 1975, page 109, abstract no. 30029x, Columbus, Ohio, US; & JP-A-74 94 723 (DAINIPPON INK AND CHEMICALS INC.) 09-09-1974 * Abstract *	1,2	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

C 09 D
C 08 L
H 01 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27-02-1987	STANGE